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USE OF ICP ATOMIC EMISSION SPECTROMETRY TO DETERMINE CONSTITUENT CONCENTRATIONS IN SOLUTION

LOS ALAMOS

QUALITY PROGRAM

APPROVAL FOR RELEASE	
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Los Alamos
Yucca Mountain Site Characterization Project

HISTORY OF REVISION

REVISION NO.	EFFECTIVE DATE	PAGES REVISED	REASON FOR CHANGE
R0	03/20/96	N/A	Initial procedure.
R1	12/23/96	2, 3, 4, 5, 6, 8, & 9	Minor non-substantive editorial changes.

USE OF INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY TO DETERMINE CONSTUTUENT CONCENTRATIONS IN SOLUTION

1.0 PURPOSE

This detailed procedure describes the use of inductively coupled plasma atomic emission spectrometry (ICP-AES) for the measurement of constituent concentrations in aqueous solutions. This DP is intended to support reactive tracer and water chemistry studies for the Yucca Mountain Project (YMP).

2.0 SCOPE

The DP applies to the analysis of any sample which is or can be converted to an aqueous form, and to those analytes whose ICP-AES detection limits are adequate for the studies proposed.

3.0 REFERENCES

LANL-YMP-QP-02.7, Personnel Training
LANL-YMP-QP-03.5, Documenting Scientific Investigations
LANL-YMP-QP-08.1, Identification and Control of Samples
LANL-YMP-QP-12.3, Control of Measuring and Test Equipment and Standards
LANL-YMP-QP-17.6, Records Management
LANL-EES-4-DP-802, Preparation of Standards for Tracer Concentration Measurements

4.0 DEFINITIONS (N/A)

5.0 RESPONSIBILITIES

The following personnel are responsible for the activities identified in Section 6.0 of this procedure:

- The Principal Investigator (PI)
- Users of this Procedure

6.0 PROCEDURE

The use of this procedure must be controlled as follows:

- If this procedure cannot be implemented as written, YMP personnel should notify appropriate supervision. If it is determined that a portion of the work cannot be accomplished as described in this DP, or would result in an undesirable situation, that portion of the work will be stopped and not resumed until this procedure is

modified, replaced by a new document, or the current work practice is documented in accordance with QP-03.5, Section 6.1.6.

- Employees may use copies of this procedure printed from the controlled document electronic file; however, employees are responsible for ensuring that the correct revision of this procedure is used.

- When this procedure becomes obsolete or superseded, it must be destroyed or marked “superseded” to ensure that this document is not used to perform work.

6.1 Principle

The ICP-AES is an analytical instrument where a sample solution is introduced into the plasma in a fine spray, generated at a uniform and reproducible rate. The intensities of the characteristic spectral lines of the elements of interest are then measured with an optical spectrometer. The relationship between light intensities and analyte concentrations is established by measuring the light emission from solutions of known concentrations (standards).

6.2 Equipment and Hardware/Software

- An ICP atomic emission spectrometer with integrated software for system control and data management. Examples include the Varian Model 220 and the Leemans Model PS 1000UV. Some systems include an optional autosampler (e.g., the Leemans Model PS 1000UV).

- Pipettes

- Volumetric Glassware/Labware

- Holding containers for standard and sample preparation

- Analytical balance for standard and sample preparation

6.2.1 Equipment Malfunctions

Any equipment failure would likely result in the shutdown of the system and inability to collect data. An exception would be plugging of the nebulizer, resulting in poor precision and a decrease in emission signal. If this should occur, it would be seen in increased standard deviations between replicates and a change in apparent concentrations of standards over time. Refer to the instrumentation manual for nebulizer cleaning procedures and for possible causes of total equipment shutdown.

6.2.2 Safety Considerations

The equipment required to carry out this procedure shall be used in accordance with applicable Los Alamos safety procedures.

Instrumentation should only be used according to the manufacturer's specifications. Safety considerations associated with handling of chemicals will depend on the chemical nature of the solutions being analyzed. Material safety data sheets (MSDSs) should be consulted to determine whether special protective clothing and/or eye protection are required. Hazardous chemical wastes should be disposed of properly.

6.2.3 Special Handling

Handling of all equipment associated with this DP should be done in accordance with manufacturer's or vendor's guidelines. Special handling of equipment or hardware should be considered on a case-by-case basis as the need arises. Any special handling should be documented in a laboratory notebook.

6.2.4 Reagent Chemicals

- Ultra-high-purity acids, such as Baker Instra-Analyzed for trace metal analysis.
- NBS/NIST standards or solutions traceable to these standards.
- Standards prepared in accordance with LANL-EES-4-DP-802, if appropriate (tracer tests).
- Double deionized water or groundwater (used to prepare solutions).

6.3 Preparatory Verification

Instrumental systems are turned on and allowed to warm up until optical checks can be performed and results are acceptable as stated in the instrumentation manuals. Elements to be determined are scanned at the emission lines to be used and compared to representative sample scans for possible interferences. Set background corrections as needed and change wavelengths if these corrections are inadequate.

6.3.1 Hold Points (N/A)

6.3.2 Calibration

The analytical balance is controlled pursuant to QP-12.3.

Prepare a mixed standard containing the elements to be determined at the desired concentrations. If possible, preparation of standards associated with tracer experiments should be done in accordance with LANL-EES-4-DP-802, Preparation of Standards for Tracer Concentration Measurements. Alternatively, standard preparation can be documented in a notebook in accordance with QP-03.5, Documenting Scientific Investigations. NBS / NIST standards or solutions traceable to these standards are controlled pursuant to QP-03.5. Because ICP-AES signals are linear over many orders of magnitude, calibration standards only need to include a blank and standard solutions containing the elements to be determined at concentrations compatible with the samples being analyzed.

Initiate the calibration sequence as described in the instrument manual, choosing at least three repetitions of each standard, and setting the scan intervals for each element to match their individual intensities. Once calibration is complete, check the standard deviations for each element to ensure they are within the expected range (<1% for elements with strong emission signals). Standard deviations for the blank will be higher, but this is expected and does not compromise the analysis.

A “check” standard is run approximately every hour during the sample analyses. Check standards should fall within a predetermined range. If this range is exceeded, recalibration will occur, and samples affected by this drift repeated.

6.3.3 Environmental Conditions

Instrumentation should be set up in a temperature controlled environment. If volume dilutions are made, samples and dilution water must be at the same temperature. Samples left at room temperature for at least one hour and deionized water stored in a carboy at room temperature are adequate.

6.4 Control of Samples

Samples, including standards, are to be identified and controlled in accordance with QP-08.1, Identification and Control of Samples. All samples should be stored in such a way that evaporation of water is minimized or eliminated during storage, by storing them in tightly capped bottles and / or refrigerating them. They should also be stored such that the impact of storage on the analyses is minimized. The sample container material should be chosen to avoid contamination and the potential sorption of constituents to the container walls. Any special procedures followed to desorb constituents prior to analyses should be documented in a laboratory notebook. If there is any question about sorption to container walls, batch sorption experiments should be conducted (and documented in a laboratory notebook) using the constituents and labware in question. Special handling requirements for different

constituents should be considered on an individual basis, and the handling and storage of all samples to be analyzed should be documented in a laboratory notebook so that a sample handling history is maintained. This documentation should be done in accordance with QP-08.1. It is imperative that sample identification and control be sufficient to trace a sample and its derivitives from its original field location to the point of analysis and that the integrity of the sample be safeguarded during the entire analytical process.

6.5 Implementing Procedure

6.5.1 Set up the ICP-AES as described in the instrumentation manual.

6.5.2 Calibrate the instrument as described in Section 6.3.2 using a blank and mixed standards with analyte concentrations in the range of those expected for the samples.

6.5.3 Dilute samples if necessary to bring them within the range of the calibration standards using dilute HNO_3.

6.5.4 If an autosampler is used, place samples and reference standards in the autosampler tray and prepare a schedule in the computer, including sample identifiers and any dilution factors that may be relevant. Set up rinse times, check standard frequencies, and calibration updates if desired.

6.5.5 Begin data acquisition as instructed in the instrument manual. Samples are run in triplicate unless otherwise requested, and data is output to a printer and/or store in the designated folder on the computer hard drive. For each set of analyses, the data are printed and included as attachments to a laboratory notebook.

6.5.6 Generate an analysis report that includes the sample identifiers and the average concentration and standard deviation of each element analyzed in each sample. Corrections are made for dilution factors recorded in the sampling schedule. The analysis report is included as an attachment to a laboratory notebook.

6.5.7 Information related to standards preparation, sample preparation, and any pertinent observations (e.g., those required by supporting DPs) needed for proper interpretation of the results are recorded in a laboratory notebook. This information is cross-referenced to the analysis report.

6.6 Data Acquisition and Reduction

Instrument operation and data acquisition/reduction are handled by a PC computer running software purchased with the instrument (e.g., Leeman Labs

PS Series Software or Varian Liberty 2.0). The software stores can print the following information: the sample identifier, element identifier which is traceable to the emission line used, each replicate reading for each element, the average reading for each element, and standard deviations for each set of replicates. Check standards are recorded as average readings with standard deviations, and the percent deviation from the calibrated value. Deviation between replicate analyses should be kept below 5% of the average value. This is dependent on the sample matrix, sensitivity of the analyte, the condition of the instrument's sample introduction system, and the software parameters used.

The PI reviews the data and associated records and determines the acceptability of the data. The PI may reject calibrations or measurements for any of the following reasons:

- anomalous results,
- instrument malfunction during the course of the calibration or measurement,
- operational deviations which call into question the accuracy of the results, and
- inadequate record keeping.

The identity of the rejected results and the basis for the rejection are recorded in the laboratory notebook and / or in the analysis report.

6.7 Potential Sources of Error and Uncertainty

6.7.1. Spectral interferences result from line overlaps and background continuums. Both may often be corrected by accounting for background on one or both sides of the peak. If possible, choose a different emission line that is free of interferences but still gives the necessary sensitivity, or use two different lines to make difficult element determinations.

6.7.2 Physical interferences occur when differences in viscosity between standards and samples cause variations in flow through the nebulizer. A buildup of salts on the nebuilzer surface will also change the flow characteristics. Dilution of samples may be necessary.

6.7.3 Chemical interferences result from molecular compound formation, and ionization and solute vaporization effects. Careful selection of the operating conditions will usually minimize any problems in this area.

6.7.4 Memory interferences occur when analytes from a previous sample contribute to current sample measurements. They result from insufficient rinsing between samples or a buildup of deposits within the spray chamber or torch assembly. Samples that have high concentrations of an element of interest should not be run before low concentration samples.

Some elements show particularly pronounced carryover even at moderate concentrations. Since the configuration of the entire sample introduction affects memory, analytes should be evaluated to determine residence times and the minimum rinse time necessary for expected concentrations. Samples that have higher concentrations can be diluted, or new rinse times determined.

7.0 RECORDS

Records generated as a result of this DP are entries in laboratory notebooks or attachments to laboratory notebooks. The documentation should consist of any applicable items identified in Section 6.0 of this procedure. Laboratory notebooks should be kept in accordance with QP-03.5.

All records should be submitted to the Records Processing Center in accordance with LANL-YMP-QP-17.6, Records Management.

8.0 ACCEPTANCE CRITERIA

Proper completion and submittal of the records described in Section 7.0 constitute the acceptance criteria for this procedure.

9.0 TRAINING REQUIREMENTS

9.1 Prior to conducting work described in Section 6.0, the user requires training to this procedure.

9.2 Training to this procedure is accomplished by “read only”. Training will be documented per QP-02.7.

10.0 ATTACHMENTS (N/A)